EXCITON POLARONS IN RUDDLESDEN-POPPER METAL HALIDES

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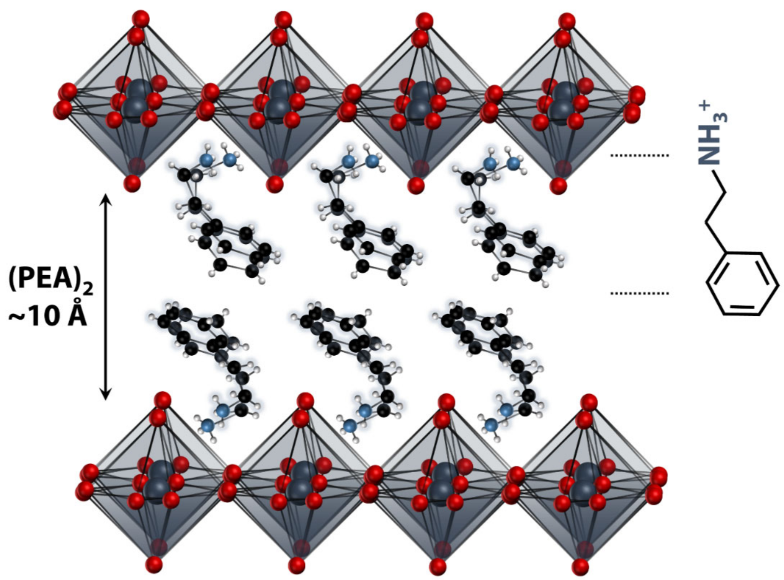
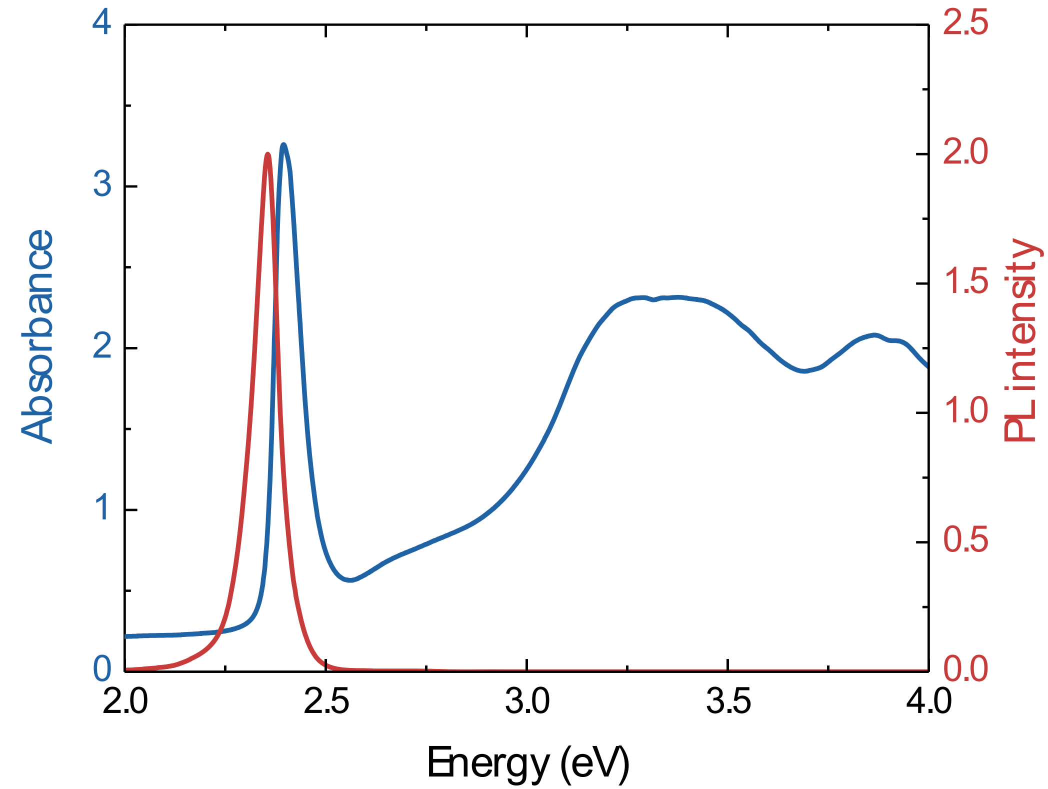
2D PEROVSKITES – OPTICAL PROPERTIES



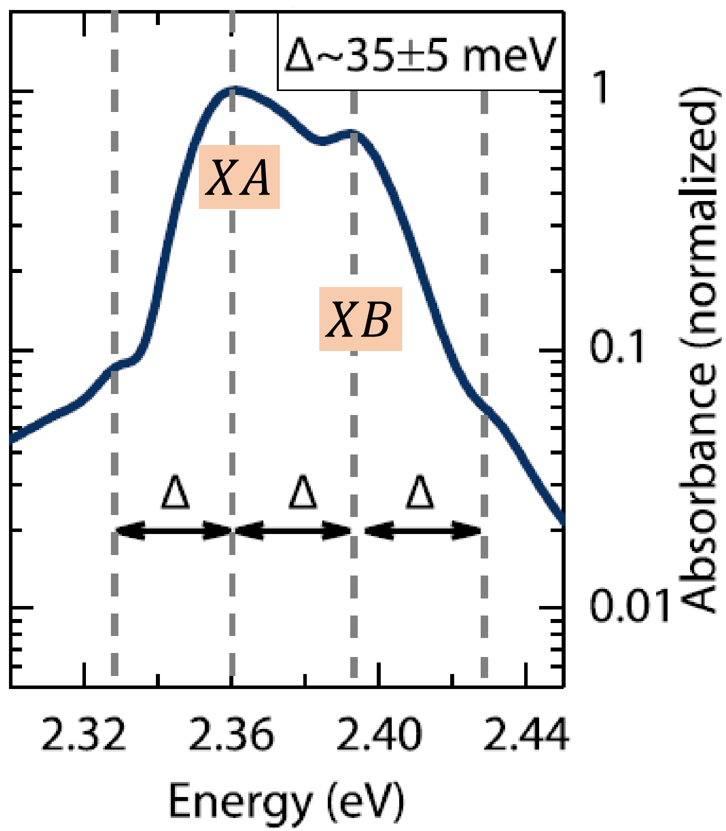
PEA: phenyl-ethylammonium

$E_B > 200\ meV$



Neutzner...Kandada, Phys. Rev. Mater. 2, 064605

$(PEA)_2PbI_4$ – EXCITONS AND SPECTRAL FINESTRUCTURE



DIVERSE CHARACTERISTICS

- Elliott analysis of exciton absorption
  Phys. Rev. Materials, 2, 064605 (2018)
- Polaronic nature of excitons:
  Nature Materials, 18, 349 (2019)
- Non-adiabatic exciton relaxation
  Chem. Materials, 31, 7085 (2019)
- Biexcitons:
  Phys. Rev. Materials, 2, 034001 (2018)
- Elastic exciton scattering:
  Phys. Rev. Research 2, 034001 (2019)
- Excitation induced dephasing:
  J. Chem. Phys, 153, 164706 (2020)
- Dark excitonic states:
  J. Mater. Chem. C. 8, 10889 (2020)

Exciton polaron Perspective:
J. Phys. Chem. Lett, 11, 3173 (2020)

MULTI-POLARON THEORY

$$\hat{H}_{e-h} = \frac{1}{N} \sum_{pkk'} U(p,k,k') e^{\dagger}_{p+k} h^{\dagger}_{p-k} h_{p-k'} e_{p+k'}$$

$$\hat{H}_{QP-ph} = \sum_{k,q} \left(\gamma_e e^{\dagger}_{k-q} e_k + \gamma_h h^{\dagger}_{k-q} h_k \right) \left(b_q + b_{-q} \right)$$

$U(p,k,k') < 0$ represents repulsive interactions and thus bipolaron problem
$U(p,k,k') > 0$ represents attractive interactions and thus **Exciton-polaron** problem

CRITERION FOR EXC-PHONON SCATTERING

$$\gamma_{1s\to 1s}(q) = \gamma_q \left(\left[1 + (\xi_e a_B q/2)^2\right]^{-2} - \left[1 + (\xi_h a_B q/2)^2\right]^{-2} \right)$$

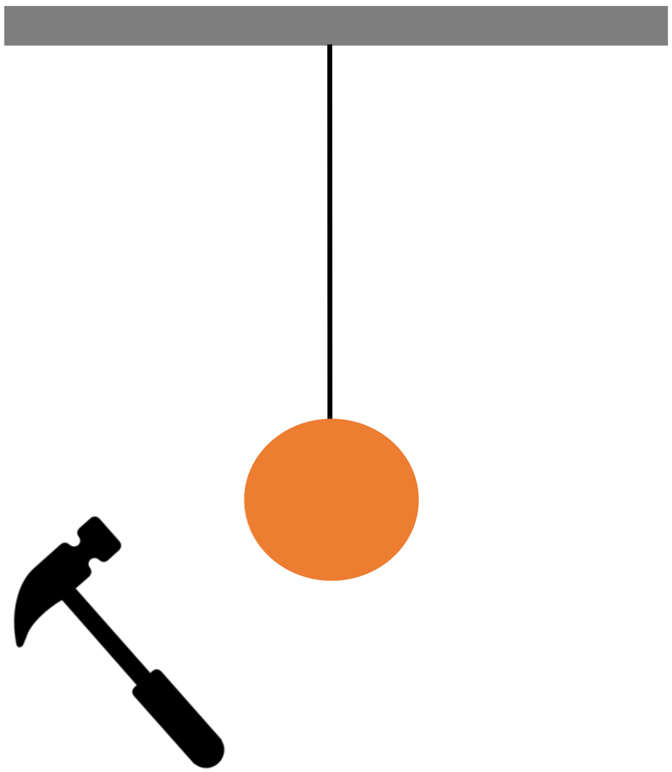
$$\xi_{e/h} = \frac{m_{e/h}}{m_e + m_h}$$

$$\underbrace{\frac{m_h}{m_e}}_{\sim\,1} \gg \underbrace{\frac{E_B}{\hbar\omega_{L0}}}_{\sim\,50} \gg \frac{m_e}{m_h}.$$

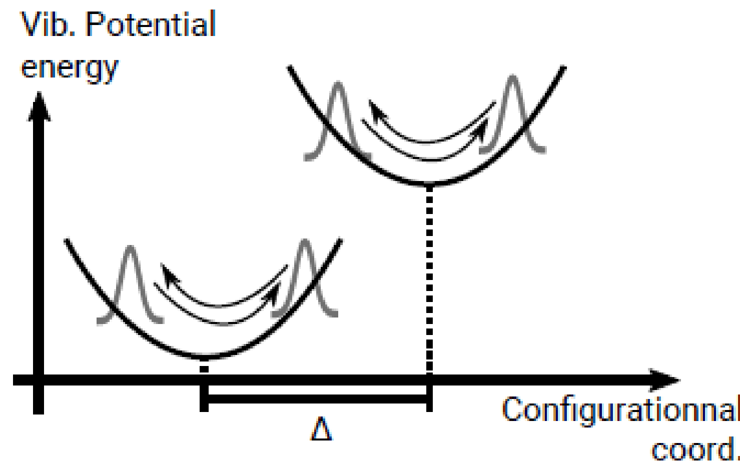
$\boxed{\text{Or do they?!}}$

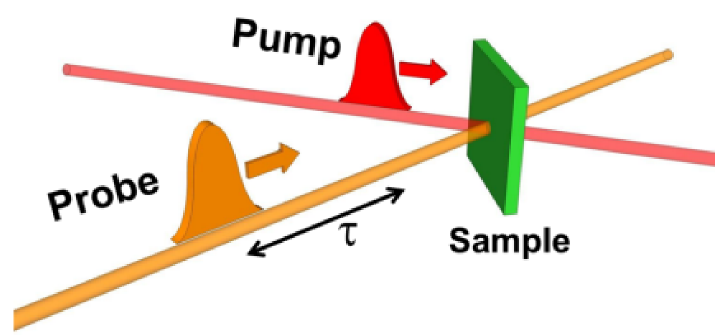
2D HOIPS **do ~~not~~** satisfy the criterion for strong exciton-phonon scattering/coupling

EXCITON LATTICE COUPLING VIA IMPULSIVE VIBRATIONAL SPECTROSCOPY

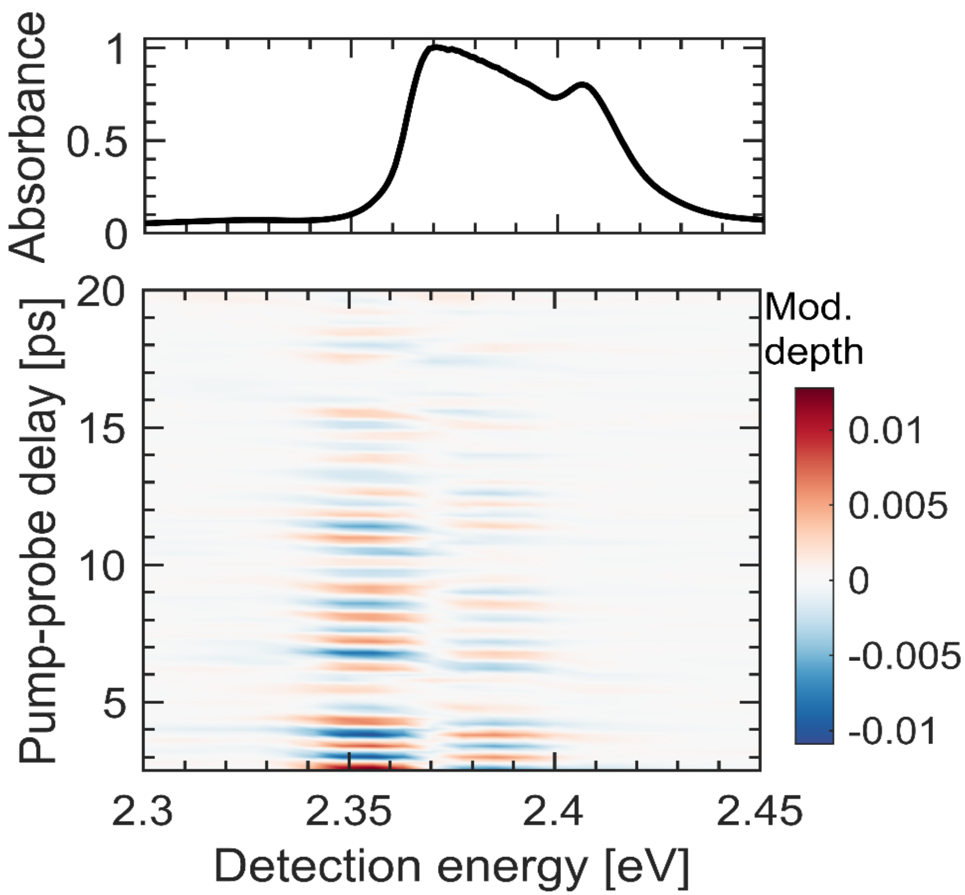


Dhar, Rogers and Nelson, Chem Rev 94, 157





EXCITON PHONON COUPLING VIA IMPULSIVE VIBRATIONAL SPECTROSCOPY



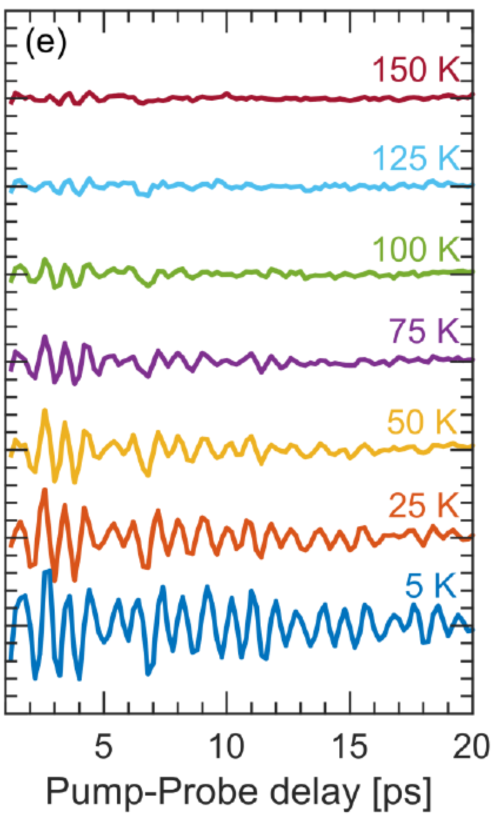
Pump : 3.1 eV
Excitation in the continuum

T = 5 K

Thouin…Kandada Nature Materials (2019)

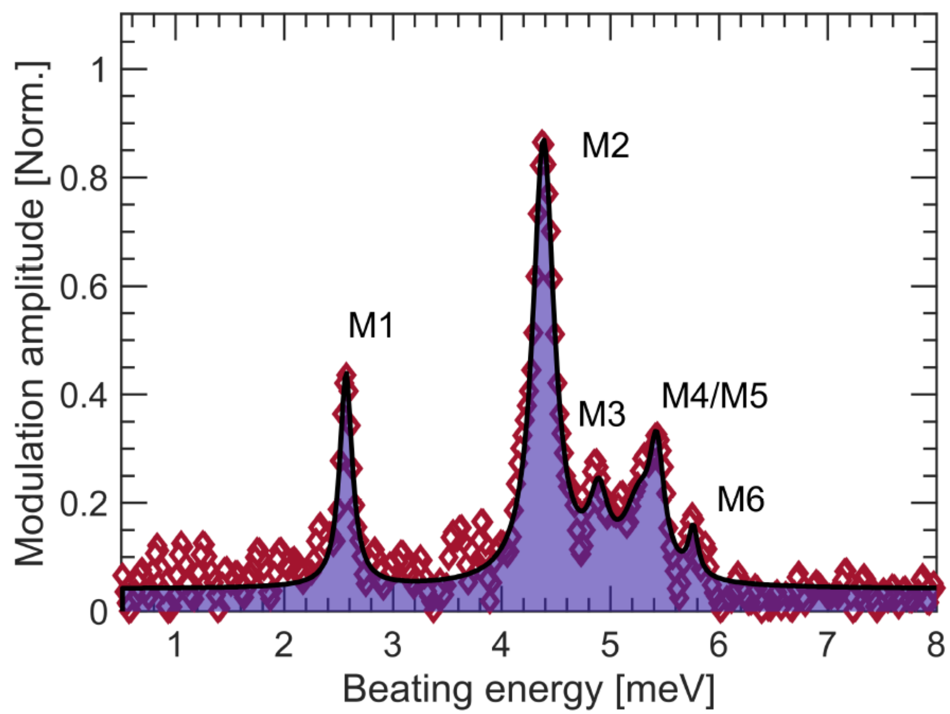
EXCITON PHONON COUPLING VIA IMPULSIVE VIBRATIONAL SPECTROSCOPY

RISRS SPECTRUM – EQUIVALENT TO RESONANT RAMAN OBTAINED VIA TIME DOMAIN MEASUREMENT

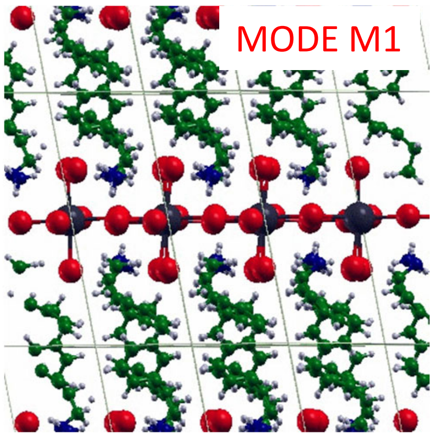


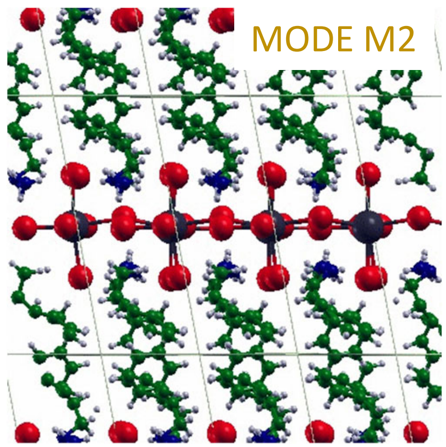
$$F(f) = \int_{-\infty}^{\infty} f(t)\, e^{-i2\pi f t} dt$$

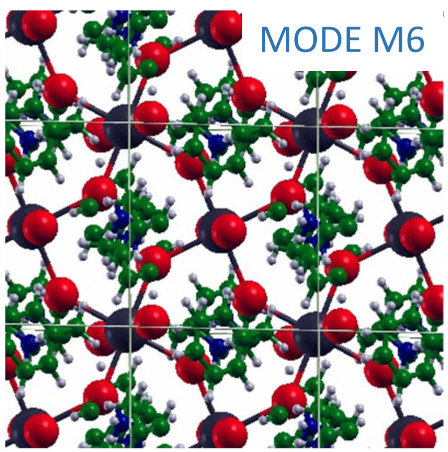
Fourier Transform

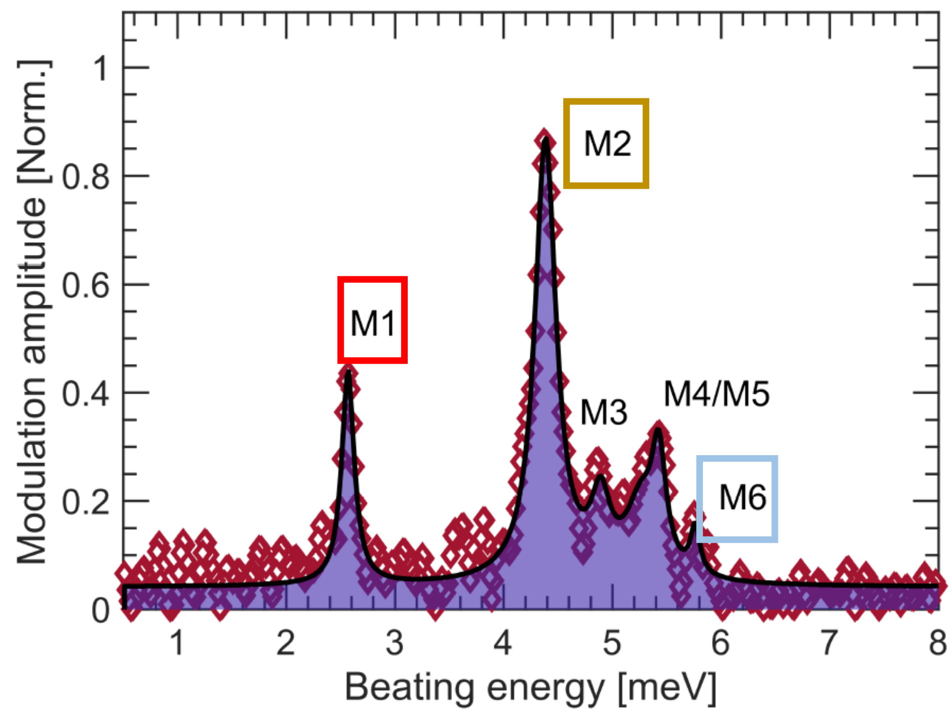


MODE ASSIGNMENT: DFT CALCULATIONS



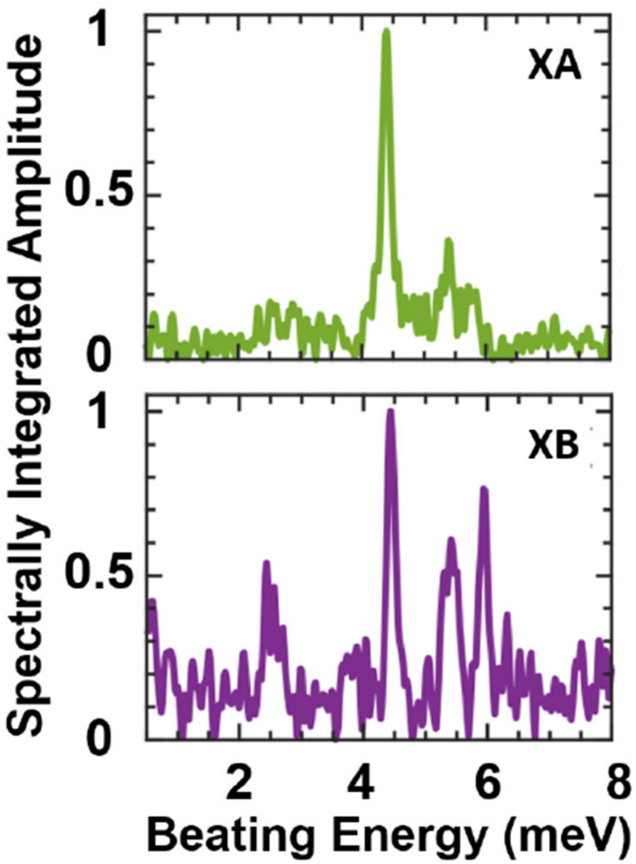


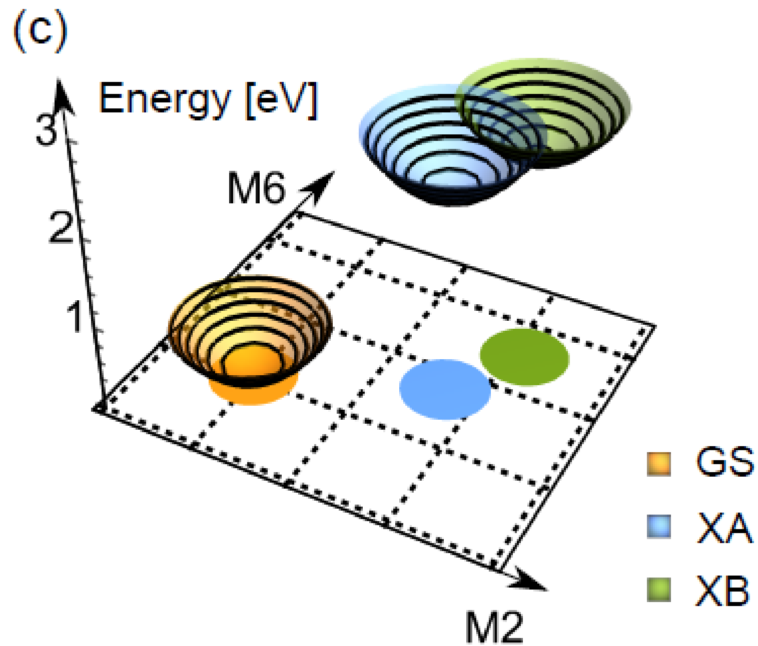




Thouin...Kandada Nature Materials (2019)

SUMMARY OF RISRS MEASUREMENTS

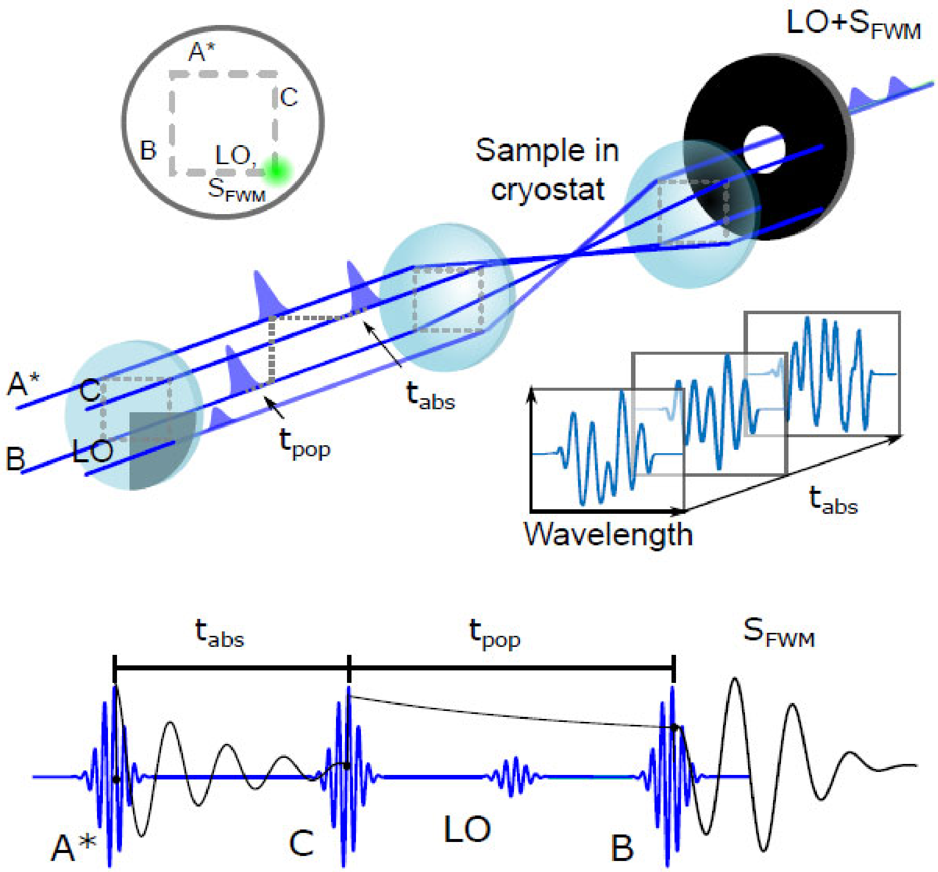


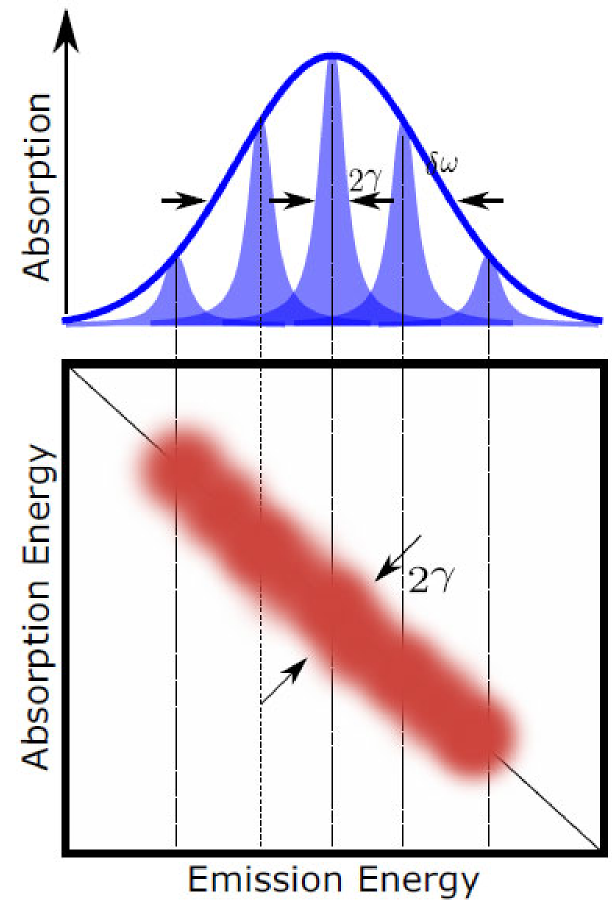


Thouin...Silva & Kandada
Nature Materials 18, 349 (2019)

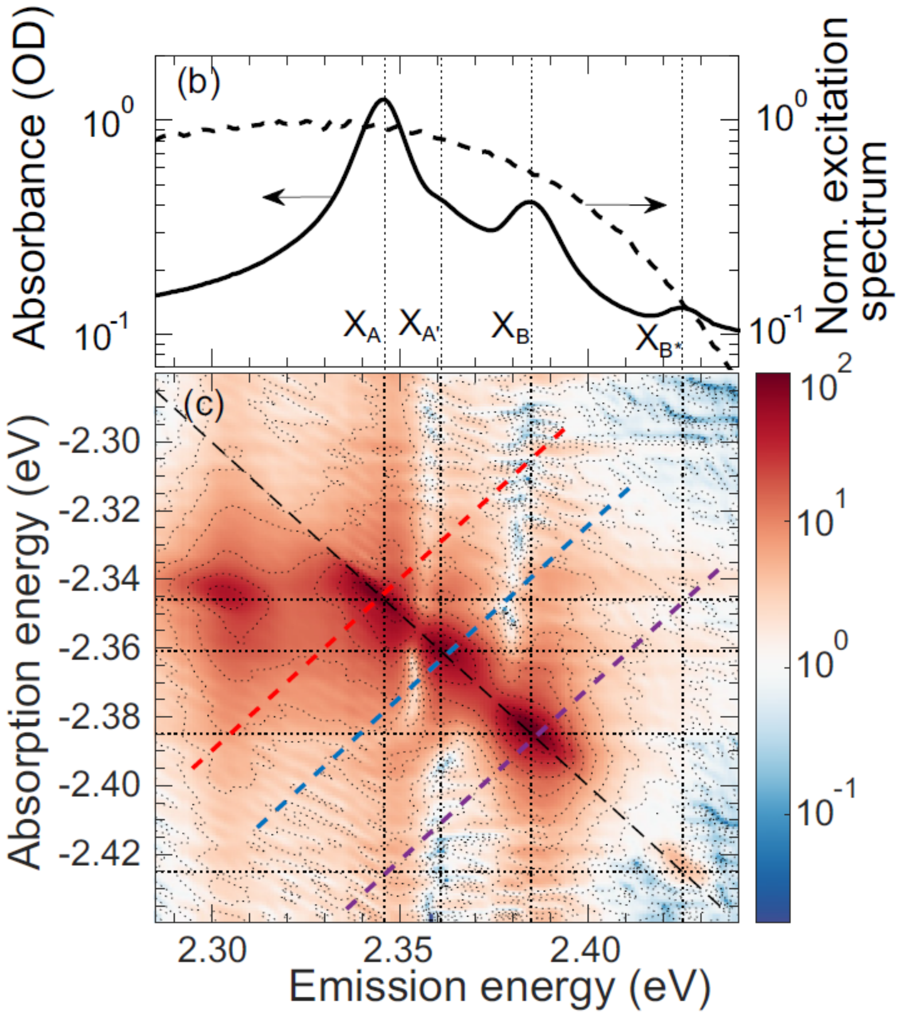
- Lattice normal modes dress distinct excitons and carriers differently
- Exciton polarons have binding energies that are offset by $\sim 35\,\mathrm{meV}$

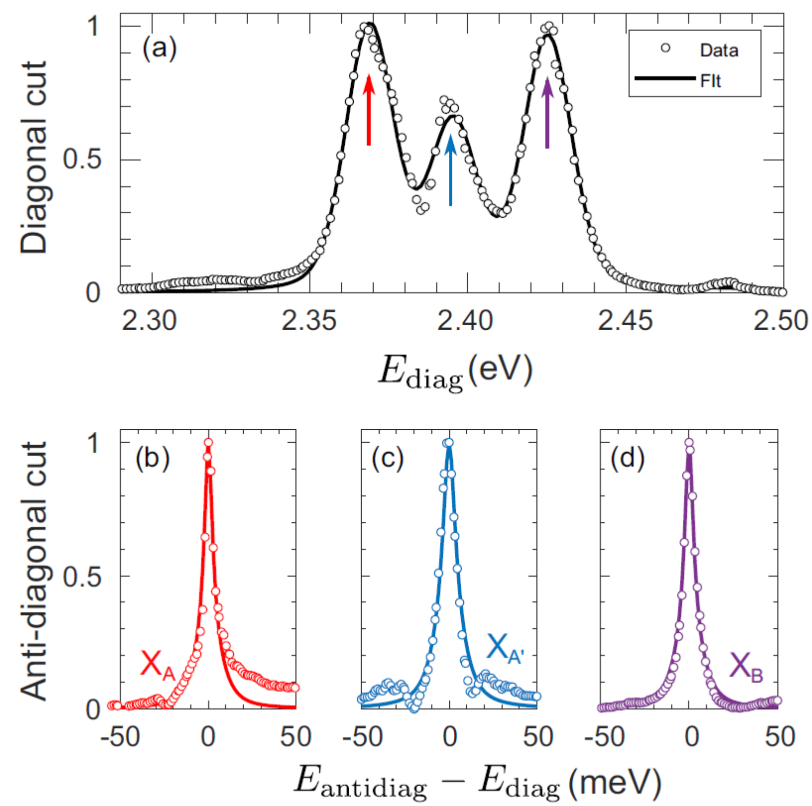
HOMOGENOUS LINEWIDTH FROM 2D SPECTROSCOPY





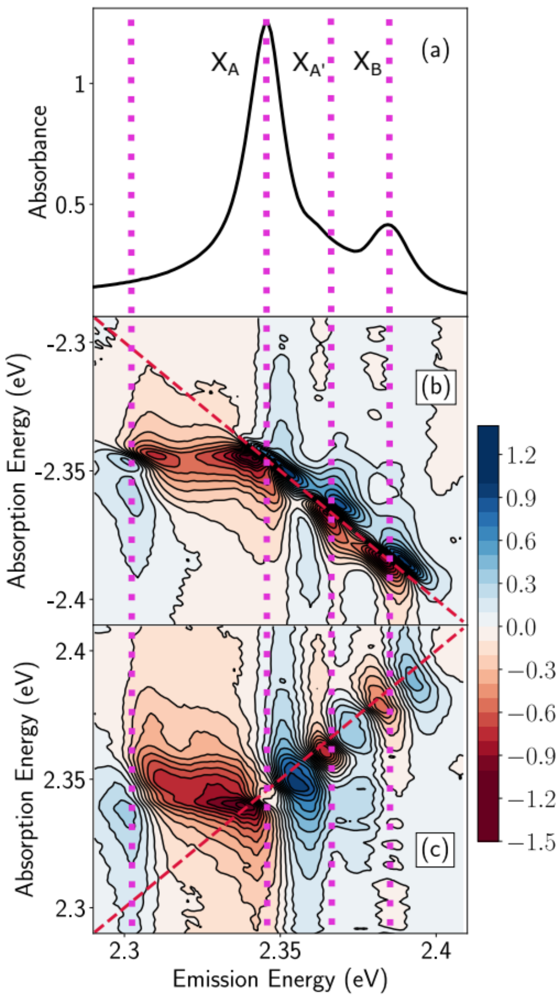
$(PEA)_2PbI_4$: EXCITON LINEWIDTH from 2D SPECTRUM

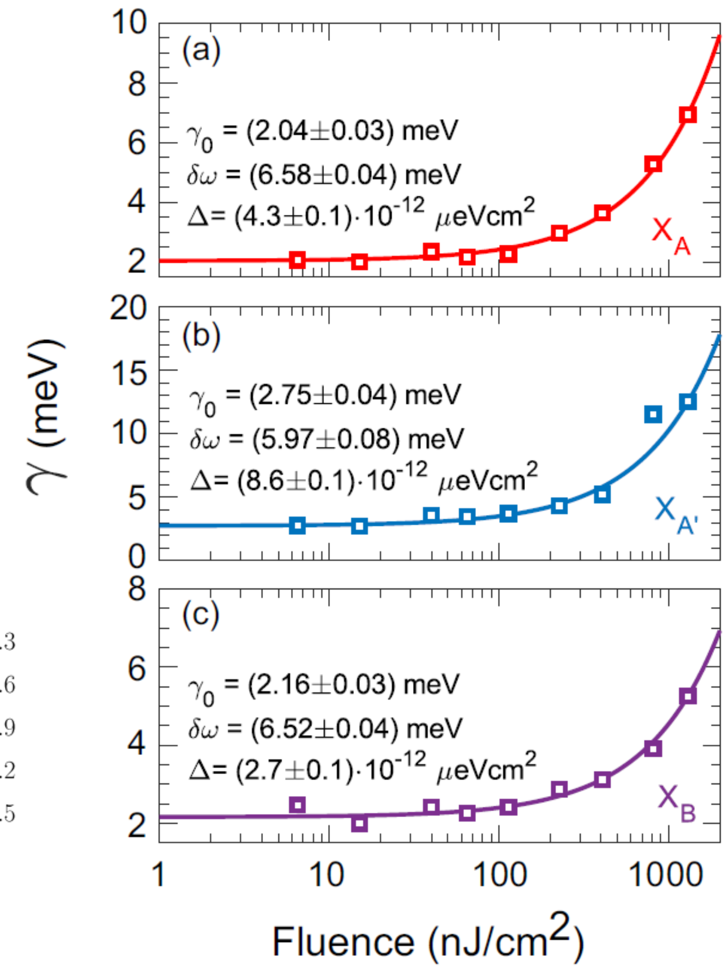




Thouin..Kandada, Silva, Phys. Rev. Research 2, 034001 (2019)

EXCITATION INDUCED DEPHASING (EID)

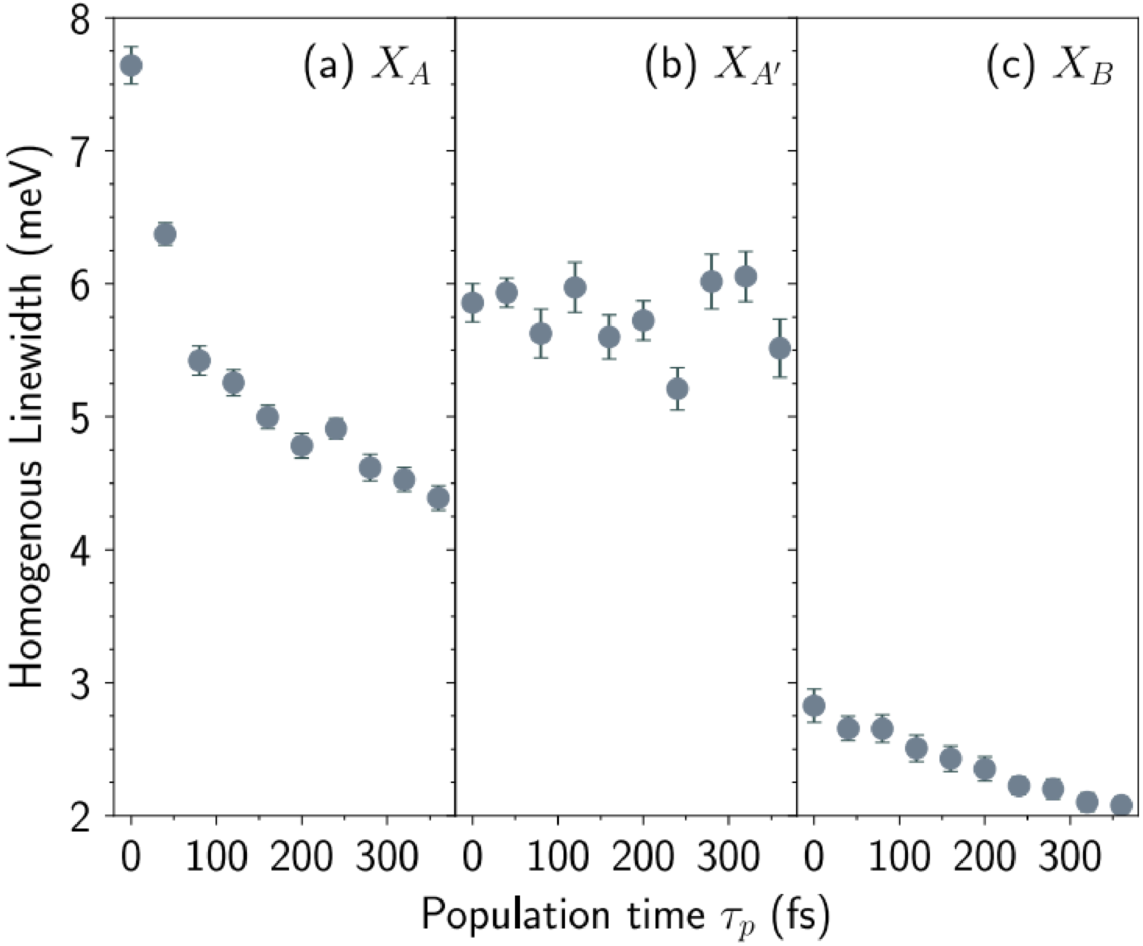


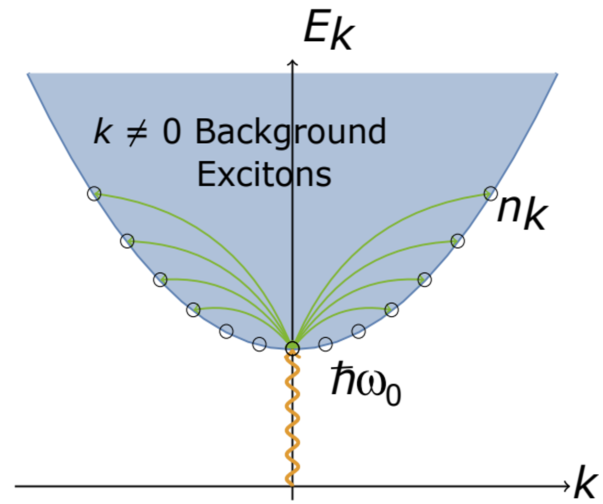


- Presence of background excitons adds to the dephasing rate.
- Manifests in the density dependence of the linewidth.
- Dispersive 2D lineshapes are a consequence of EID.

Thouin..Kandada, Silva, Phys. Rev. Research 2, 034001 (2019).
Kandada et al, J. Chem. Phys.

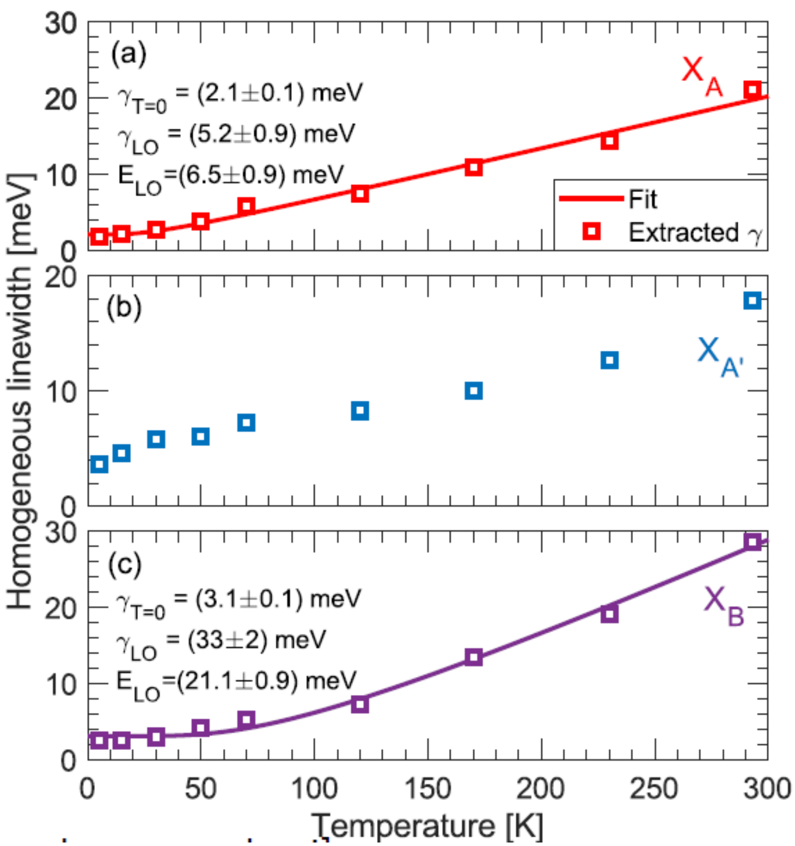
TIME DEPENDENT LINEWIDTH AND EID



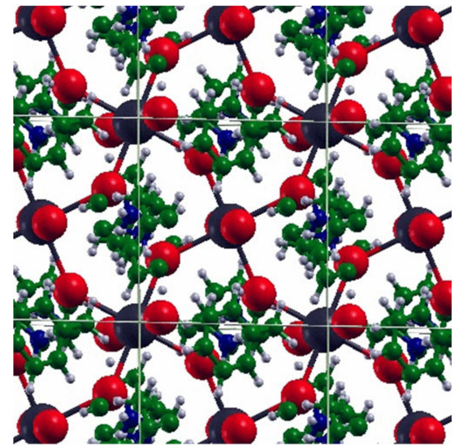


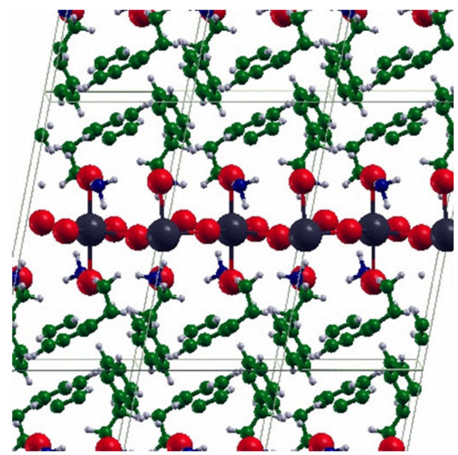
Kandada et al, J. Chem. Phys. 153, 154115

TEMPERATURE DEPENDENCE OF LINEWIDTH – PHONON SCATTERING



Thouin..Kandada, Silva, Phys. Rev. Research 2, 034001 (2019)

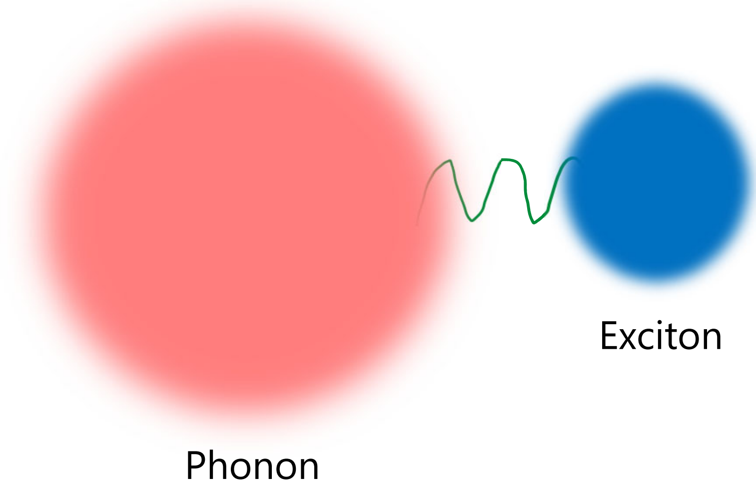




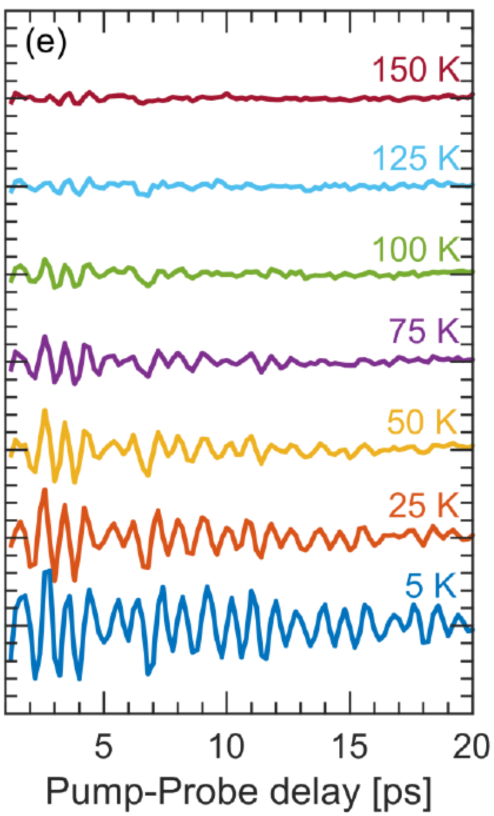
?!

What is the importance of the phonon-phonon scattering in exciton dephasing?

- Critical to the verification of the exciton polaron hypothesis



PHONON DEPHASING TIME



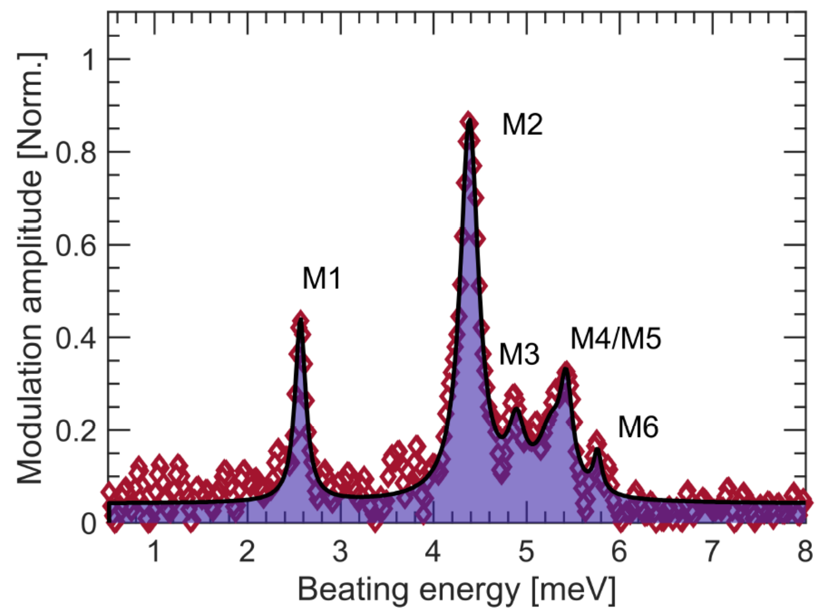
$$F(f) = \int_{-\infty}^{\infty} f(t)\, e^{-i2\pi f t} dt$$

Fourier Transform

Wavelet Transform

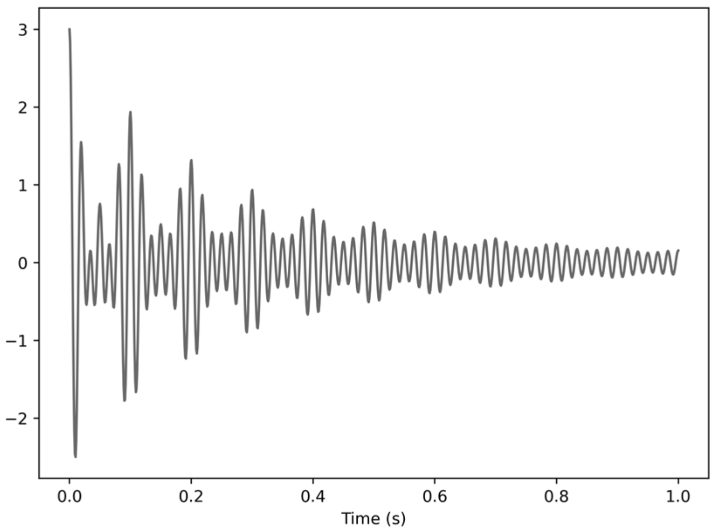
$$W(\tau, s) = \frac{1}{\sqrt{|s|}} \int_{-\infty}^{\infty} f(t)\, \psi^* \left(\frac{t-\tau}{s}\right) dt$$

$$\psi(t) = \frac{1}{\sqrt{\pi \mathrm{B}}}\, e^{-\frac{t^2}{B}}\, e^{i2\pi t}$$ Complex Morlet Wavelet



Example. Generic Damped oscillation

$$f(t) = e^{-2t}\sin(120\pi) + e^{-4t}\sin(100\pi) + e^{-8t}\sin(80\pi)$$

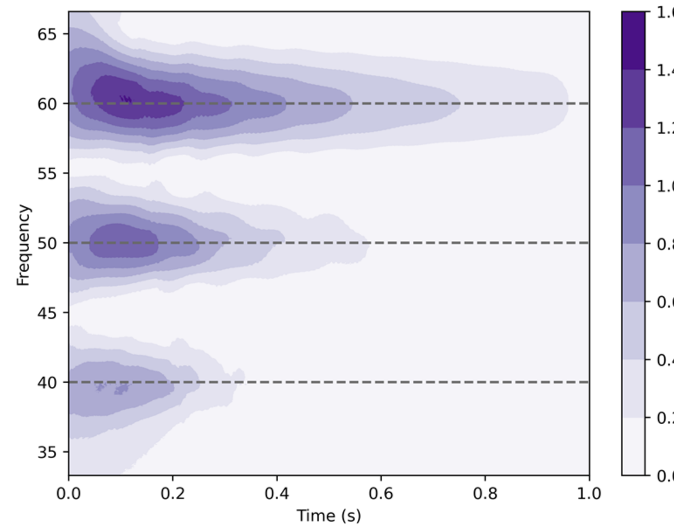


Wavelet Transformation

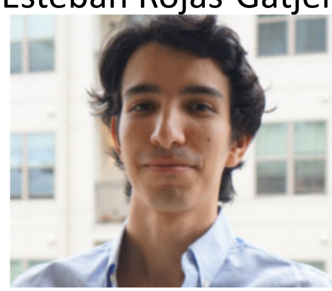
Using PyWavelet Package

Wavelet: Complex Morlet

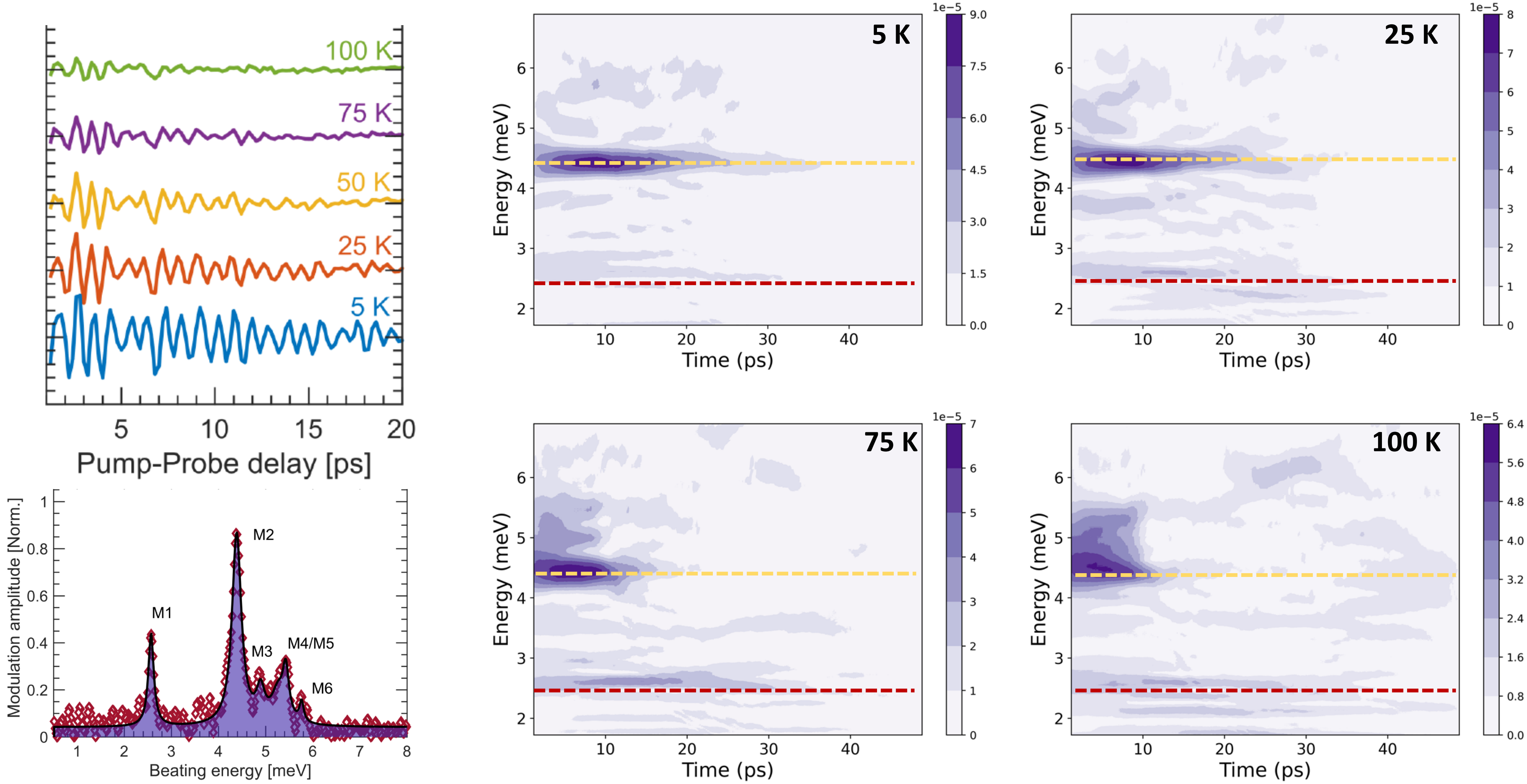
$|W|$



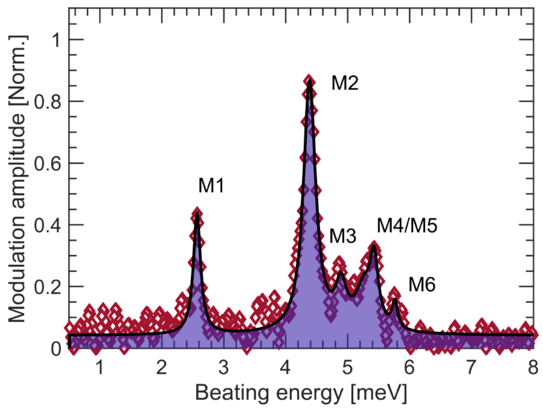
Esteban Rojas-Gatjens



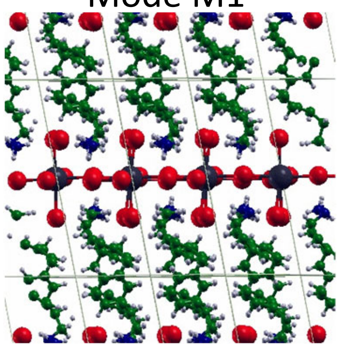
WAVELET ANALYSIS



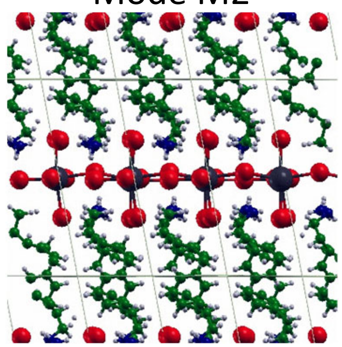
PHONON DEPHASING RATE



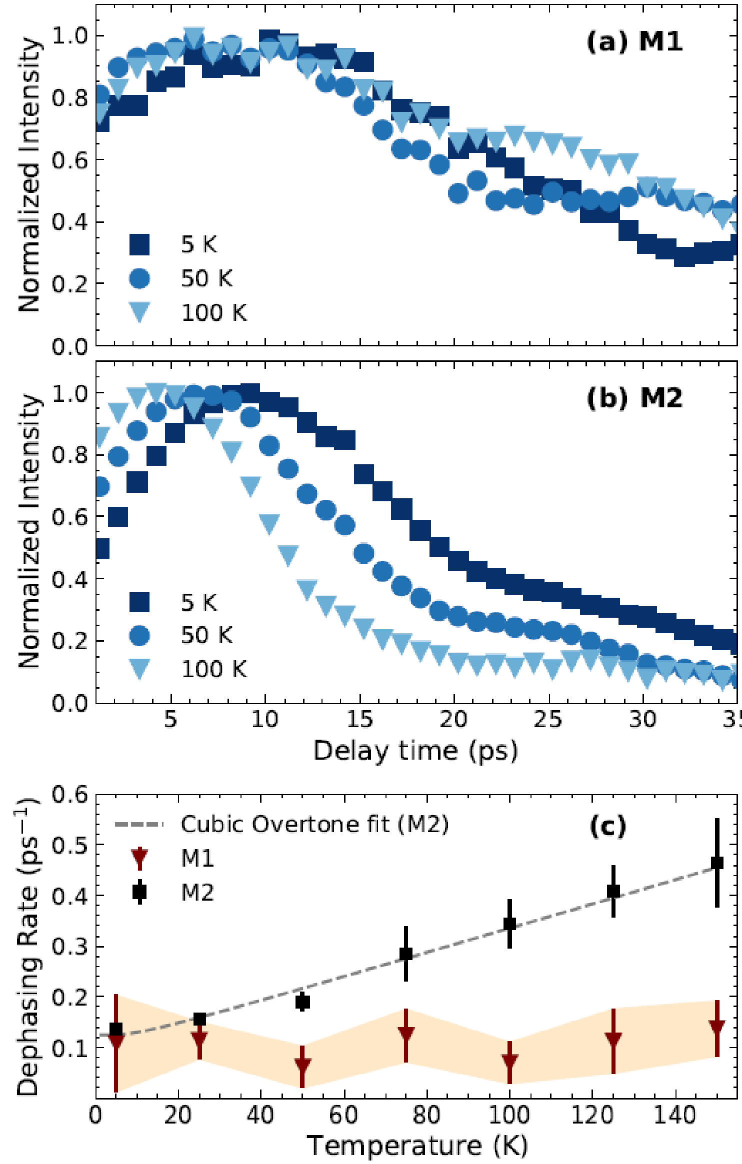
Mode M1



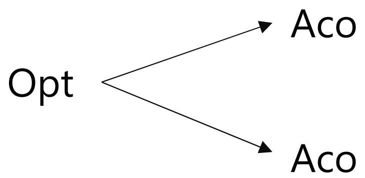
Mode M2



M2 exhibits anharmonicity.
M1 dynamics independent of temperature



PHONON DEPHASING RATE



$$\Gamma = \Gamma_0 + \gamma_0 \left[1 + \frac{2}{\exp\left(\frac{\hbar\omega}{2k_B T}\right) - 1} \right]$$

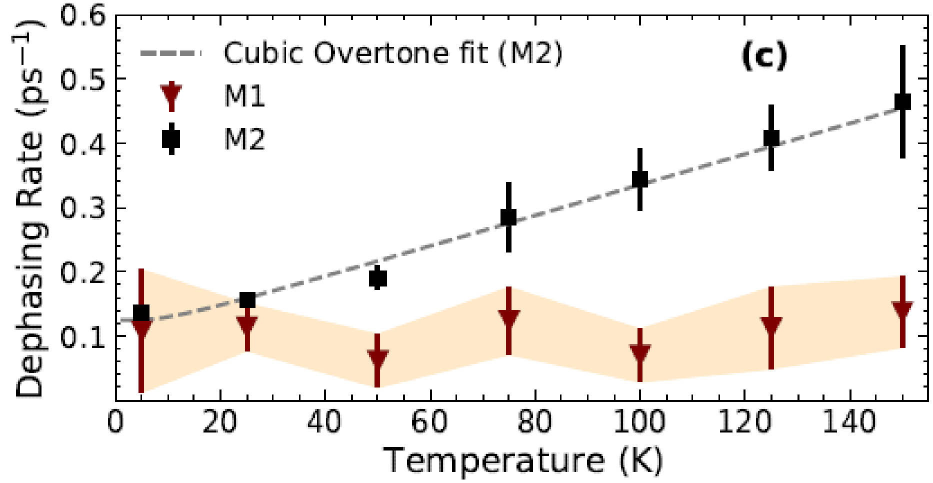
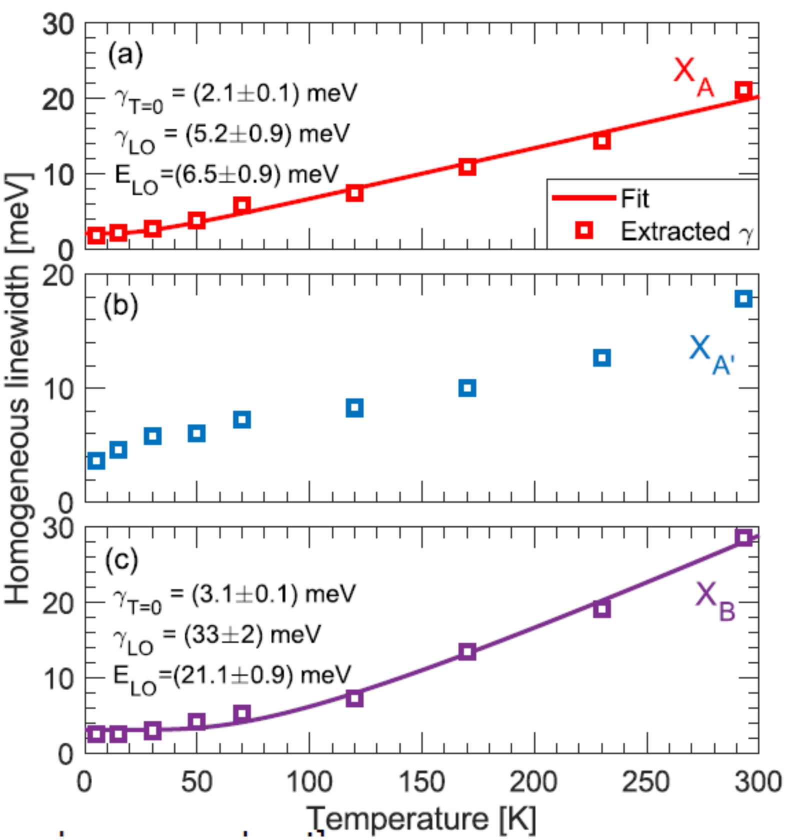


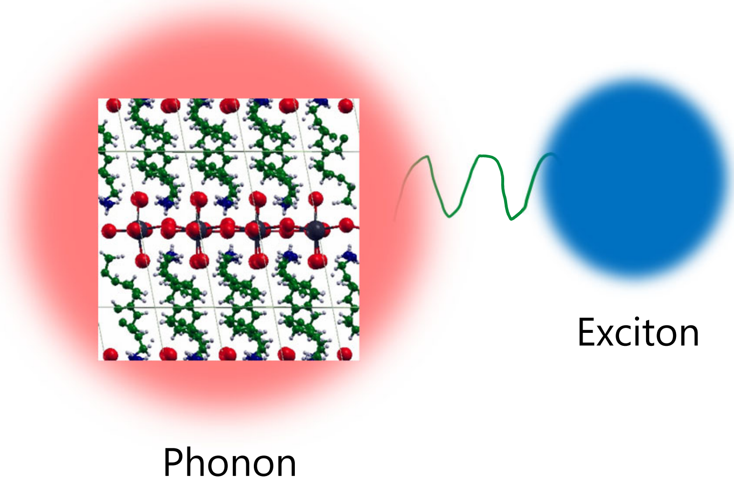
Table 1 Comparison between anharmonic constants for different materials reported in the literature.

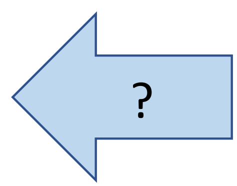
Material	Energy (meV)	$\gamma_0 \times 10^{-2}$ (ps^{-1})	Ref
$CsPbCl_3$ NCs	4.46	1.5	19
	9.42	4.8	
	11.78	4.2	
MoS_2	47.6	1.6	21
$SrTiO_3$	5.58	8.0	22
	1.65	1.5	
GaAs	36.6	11	23
$(PEA)_2PbI_4$	4.40	3.0 ± 0.5	This work

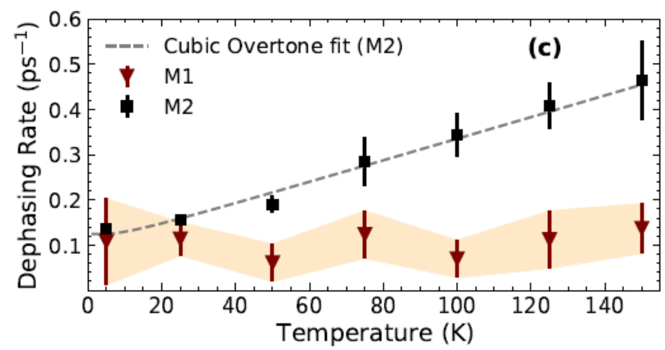
What is the importance of the phonon-phonon scattering in exciton dephasing?

- Critical to the verification of the exciton polaron hypothesis

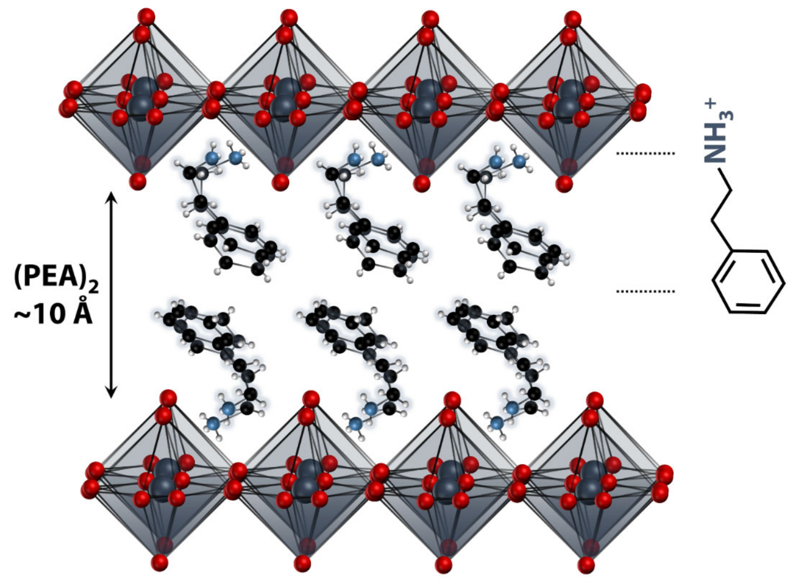






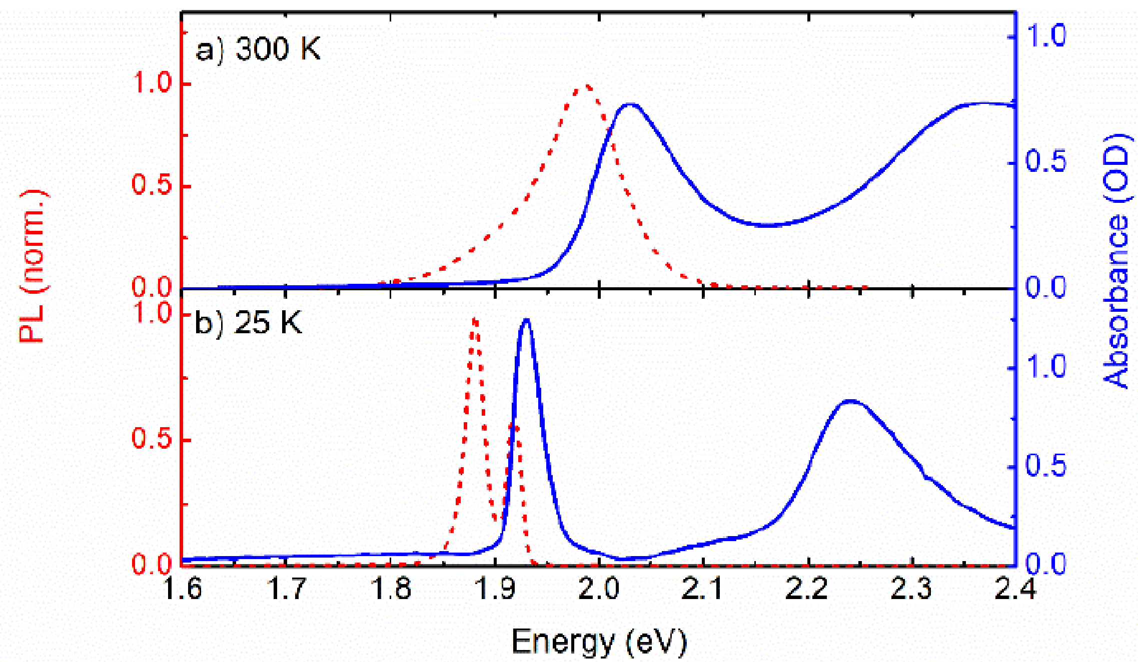


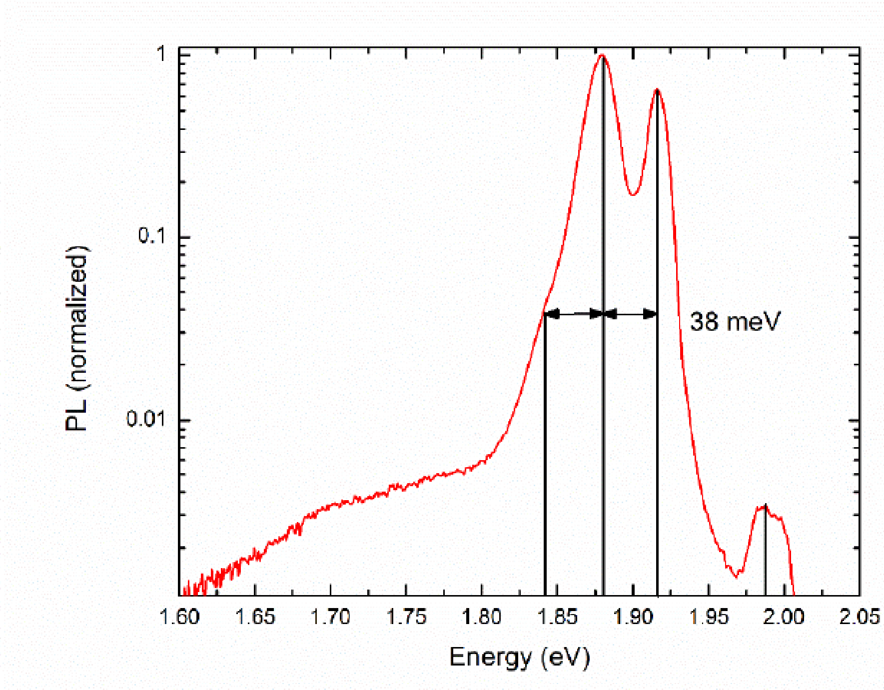
2D PEROVSKITES – OPTICAL PROPERTIES AND THE METAL CATION



2D PEROVSKITES – OPTICAL PROPERTIES AND THE METAL CATION

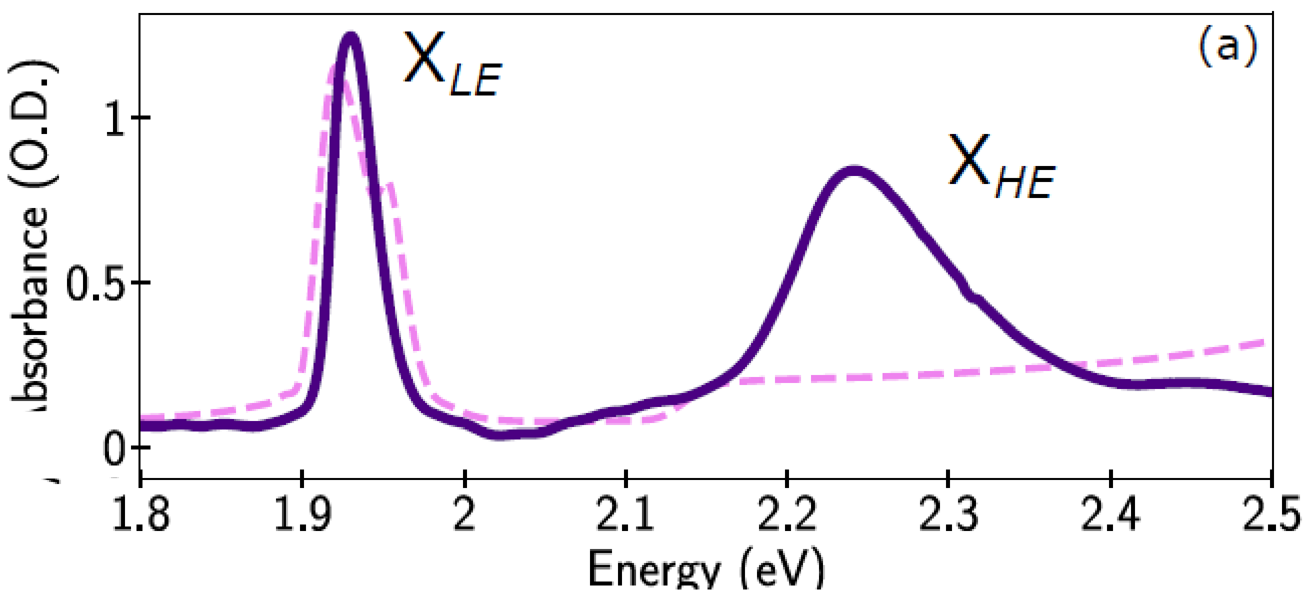
Exciton finestructure exists also in the tin derivatives.





Folpini....Kandada, J. Mater. Chem. C 8, 10889 (2020)

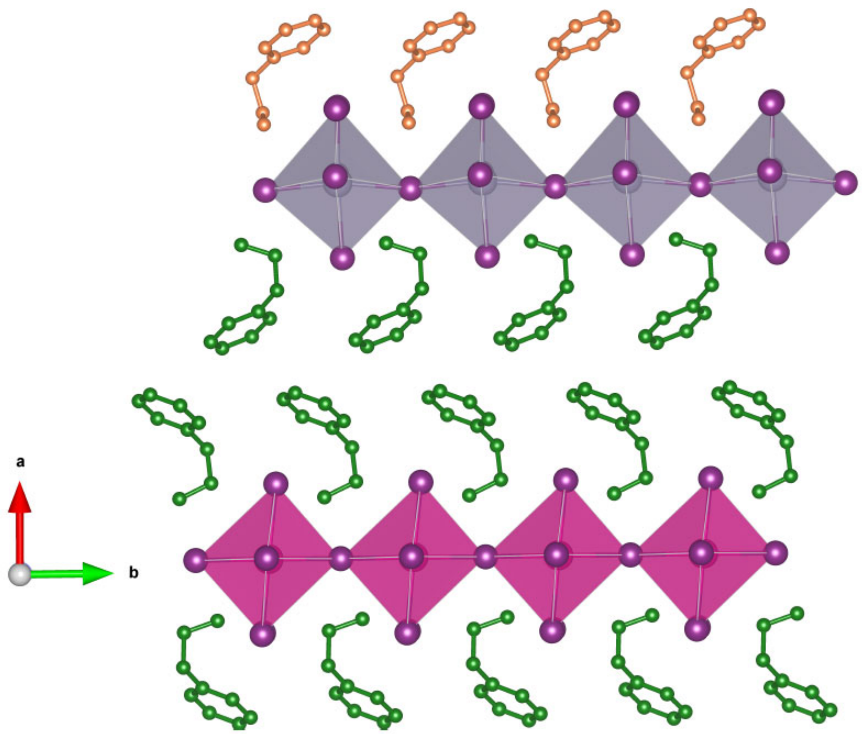
2D PEROVSKITES – OPTICAL PROPERTIES AND THE METAL CATION

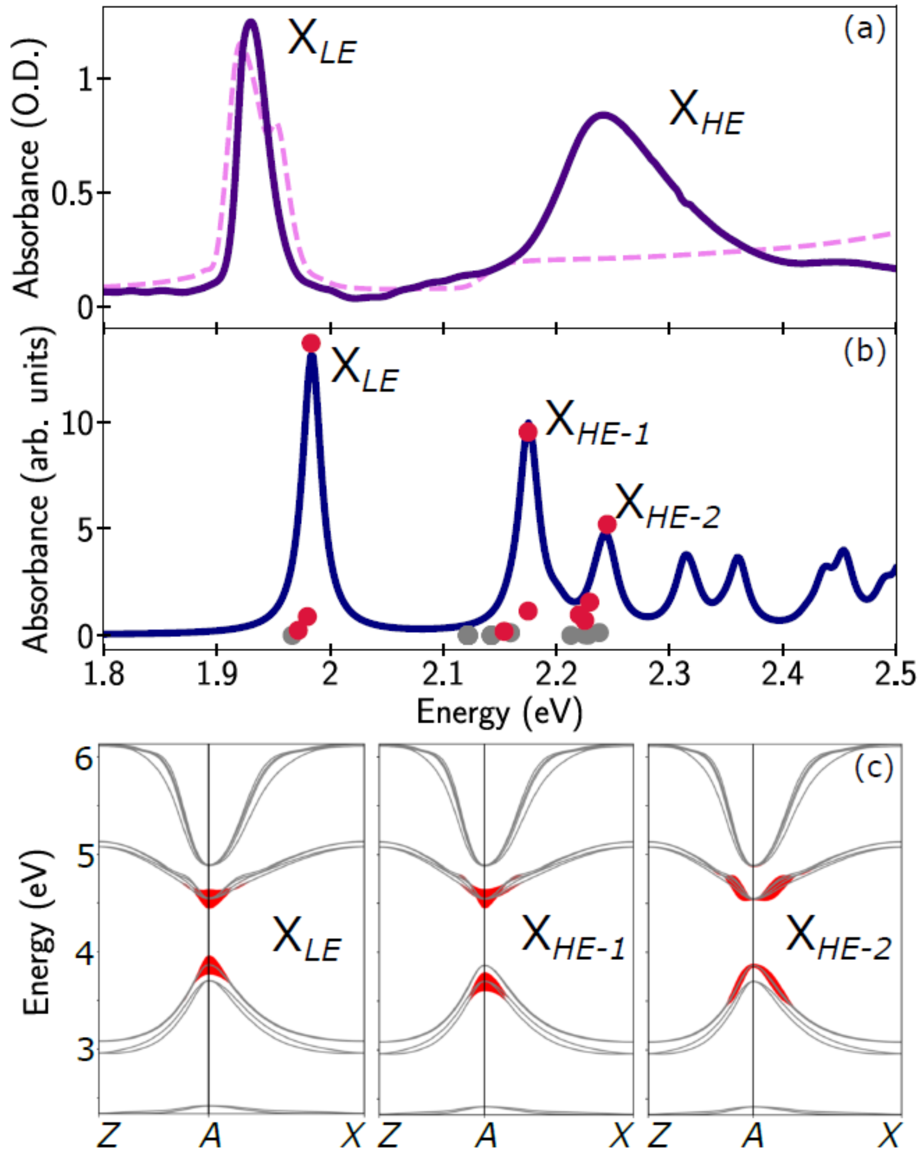


There are multiple resonances in the linear absorption spectrum which were absent in the spectrum of the lead derivative.

Folpini….Kandada, ChemrXiv (2021)

2D TIN PEROVSKITES



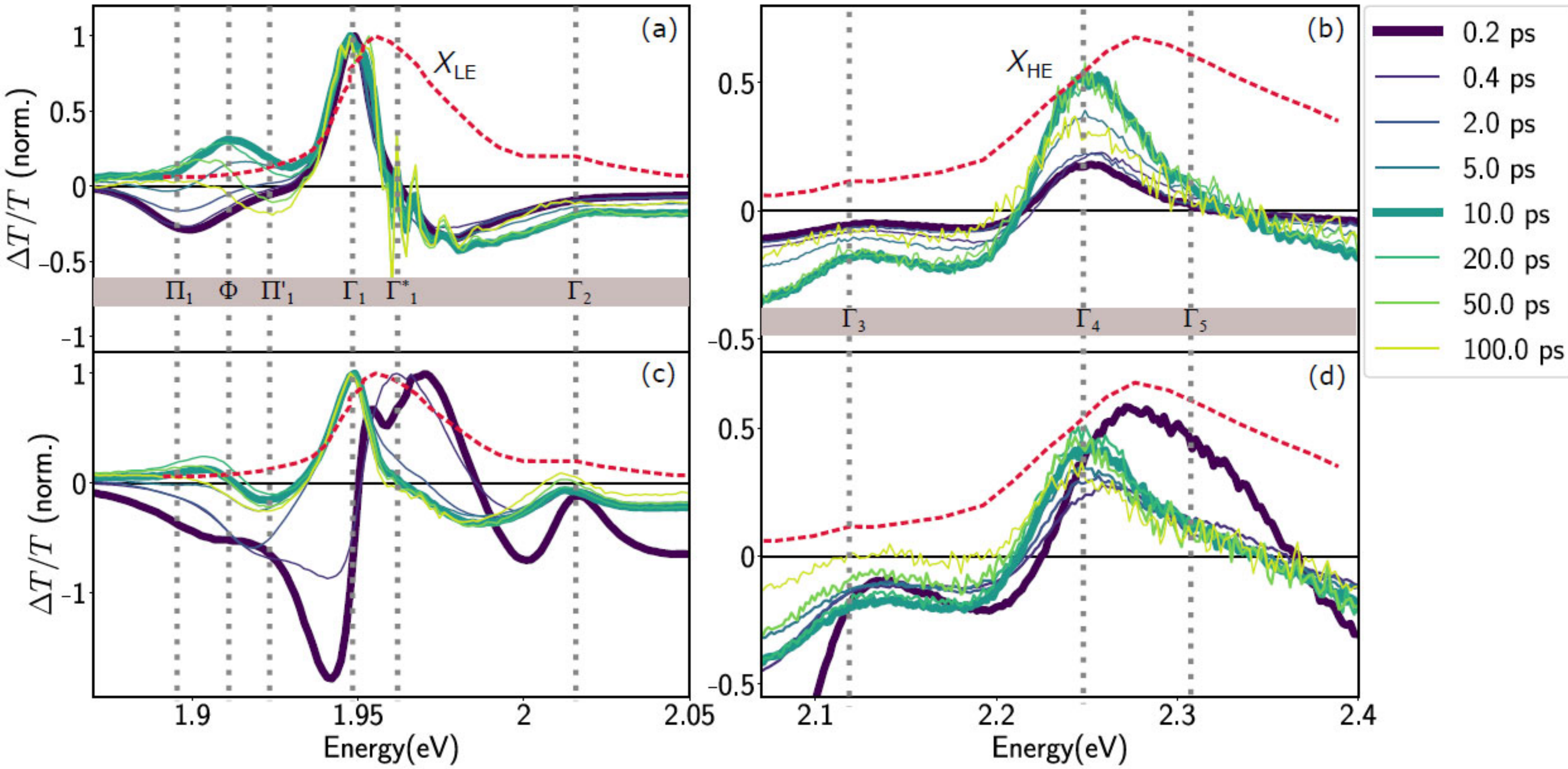


- Two stable lattice deformations due to enhanced organic-inorganic interactions.
- This leads to the splitting of the valence bands and two exciton series

2D TIN PEROVSKITES – TRANSIENT ABSORPTION

Resonant X_{LE}

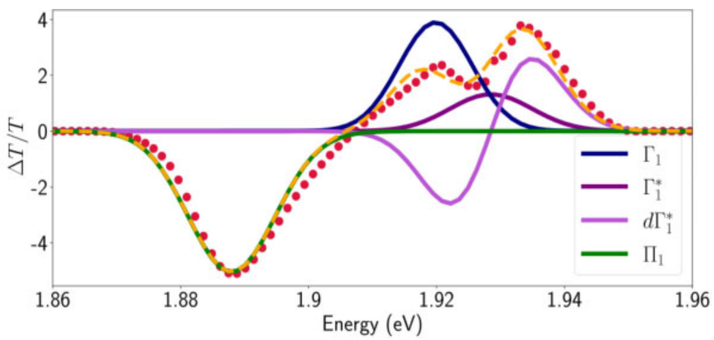
Hot carriers



Folpini....Kandada, ChemrXiv (2021)

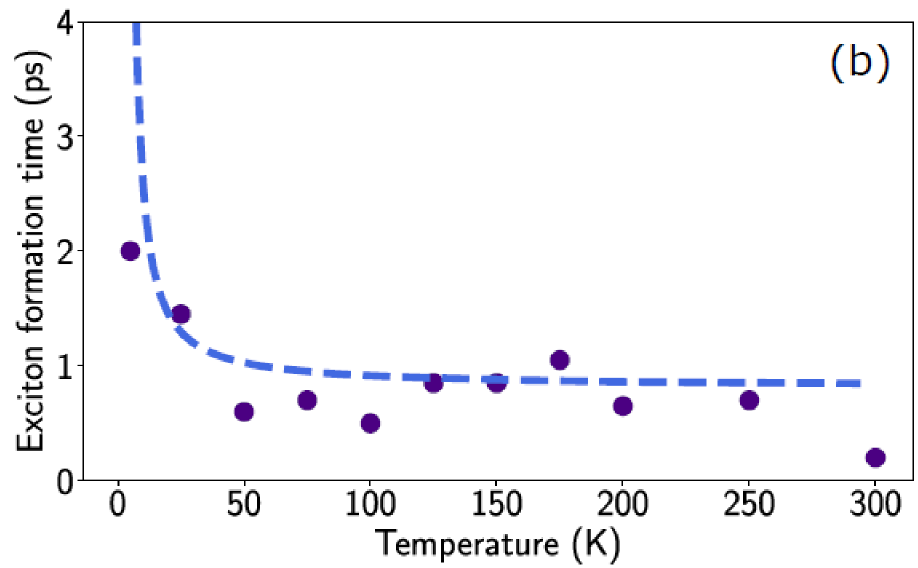
Clear signatures of carrier thermalization and exciton formation

EXCITON FORMATION DYNAMICS



Exciton formation is assisted by LO phonon scattering

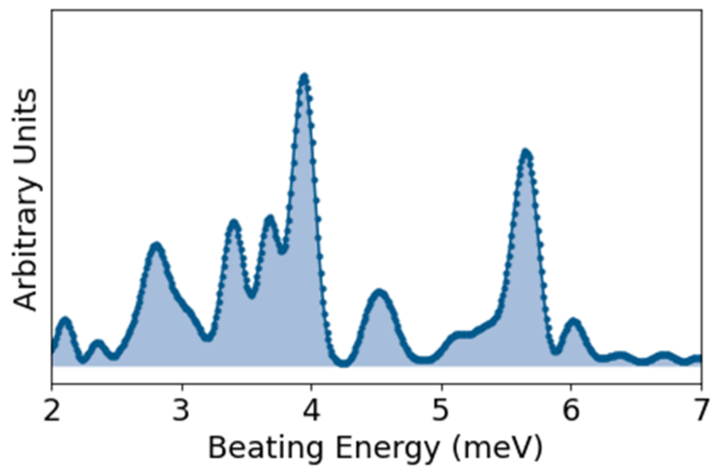
$$\tau_{therm} \propto \exp\left(-\frac{E_{ph}}{kT}\right)\ ; E_{ph} \sim 4\ meV$$

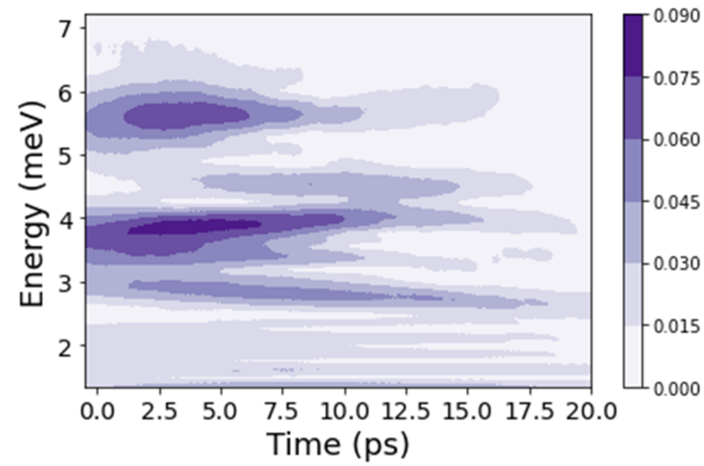


Folpini....Kandada, ChemrXiv (2021)

PHONON DYNAMICS LEAD Vs TIN

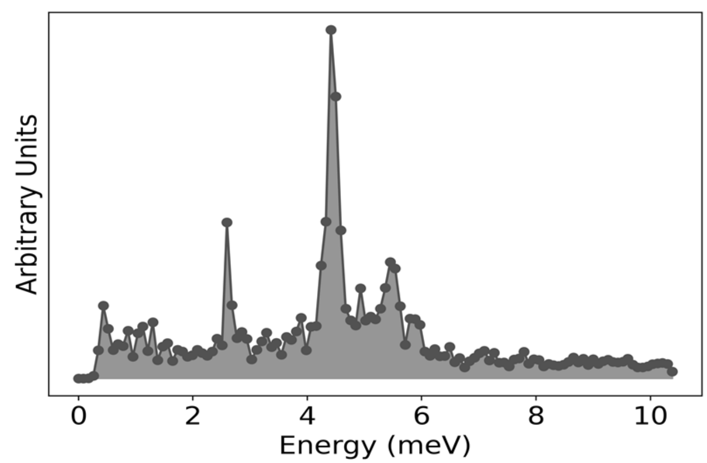
PEA_2SnI_4

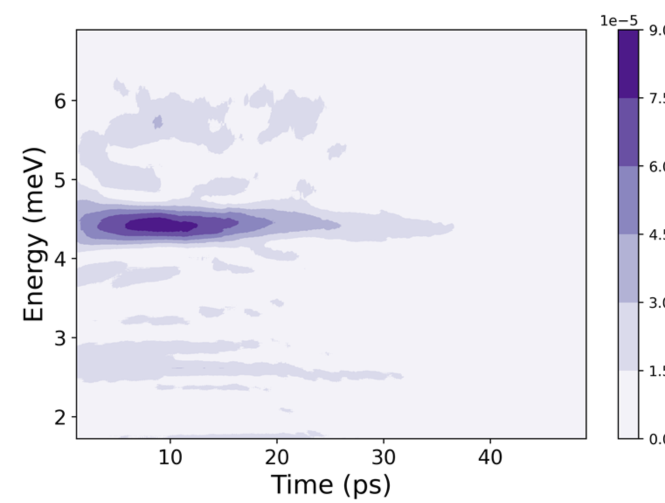




Similar phonon energies, from the halogen.

Richer spectrum – due to the lattice deformations

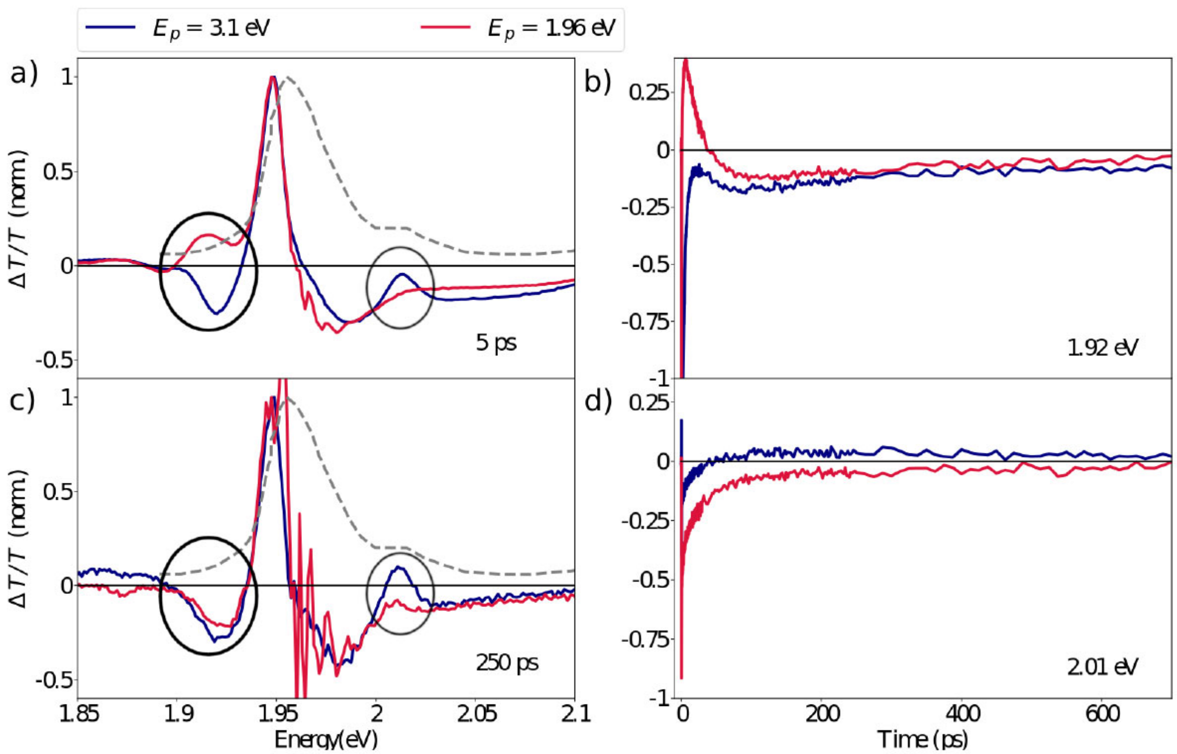




PEA_2PbI_4

X_{HE} IS A POPULATION RESERVOIR

- X_{LE} formation is not complete within a few picoseconds



WHAT DO WE KNOW SO FAR?

- Excitons in 2D hybrid metal halides are coupled to the phonons resulting in a spectral finestructure
- The finestructure is NOT composed of phonon-replicas: Distinct excitons
- Exciton-exciton many-body scattering reflects the different lattice dressing of the excitons
- Thermal dephasing of excitons – beyond (simple) exciton-LO phonon scattering
- Peculiar phonon-phonon interactions contributes to the exciton dephasing
- Population relaxes through the multiple exciton states via non-adiabatic coupling to the anharmonic phonons
- Metal cation does NOT have significant role in the phonon structure, apart from a few differences due to lattice deformations.

TAKE-HOME MESSAGE

- Excitons in 2D hybrid metal halides are EXCITON POLARONS